

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

NASA TECHNICAL MEMORANDUM

NASA TM X-73380

(NASA-TM-X-73380) BULK AND THIN FILMS OF
FeTe: A MOESSBAUER STUDY (NASA) 30 p HC
A03/MF A01 CSCL 20L

N77-23965

Unclas

G3/76 29061

BULK AND THIN FILMS OF FeTe: A MÖSSBAUER STUDY

By W. T. Escue, Kamna Aggarwal,
and R. G. Mendiratta
Electronics and Control Laboratory

February 1977

NASA



*George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama*

1. REPORT NO. NASA TM X-73380	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE Bulk and Thin Films of FeTe: A Mössbauer Study		5. REPORT DATE February 1977	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) W. T. Escue, Kamna Aggarwal,* and R. G. Mendiratta*		8. PERFORMING ORGANIZATION REPORT #	
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		10. WORK UNIT NO.	
		11. CONTRACT OR GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D. C. 20546		13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES Prepared by Electronics and Control Laboratory, Science and Engineering *Physics Department, Indian Institute of Technology, Delhi, New Delhi-110029, India.			
16. ABSTRACT Bulk and thin films of FeTe have been studied Mössbauer spectroscopically. It was found that FeTe has one noncubic Fe ²⁺ site which is 3d ² 4s 4p ³ hybridized. The presence of dangling bands is indicated in spectra of FeTe thin films. The films show a tendency of texture formation. The substrate is observed to influence the film structure and nature of bonds in films.			
17. KEY WORDS		18. DISTRIBUTION STATEMENT Unclassified — Unlimited <i>W. T. Escue</i>	
19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 31	22. PRICE NTIS

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. EXPERIMENTAL DETAILS	3
A. Sample Preparation and Characterization	3
B. Results and Discussion	6
REFERENCES	25

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	Photograph of x-ray diffraction pattern of bulk FeTe	3
2.	Transmission electron diffraction pattern of thin film of FeTe (500 Å thickness)	5
3.	Mössbauer spectrum of bulk FeTe	7
4.	Mössbauer spectrum of FeTe film 80 Å (freshly deposited)	9
5.	Mössbauer spectrum of FeTe film 180 Å (freshly deposited)	10
6.	Mössbauer spectrum of FeTe film 730 Å (freshly deposited)	11
7.	Mössbauer spectrum of FeTe film 2000 Å (freshly deposited)	12
8.	Mössbauer spectrum of FeTe 4000 Å (freshly deposited)	13
9.	Variations of IS and QS values with film thickness	16
10.	Thickness variation of line width asymmetry of the doublets	18
11.	Variation of W_1 with film thickness	20
12.	Mössbauer spectrum of FeTe film 500 Å (deposited on aluminum substrate)	22
13.	Mössbauer spectrum of FeTe film 1000 Å (deposited on aluminum substrate)	23

BULK AND THIN FILMS OF FeTe: A MÖSSBAUER STUDY

I. INTRODUCTION

Until the last century, the study of solids was confined to the investigation of their bulk properties, and the concept of solid state implied a periodic array of atoms having a long-range order. These bulk studies on the average showed definite predictable and reproducible results.

Thin-film studies were handicapped in the past because of the lack of good vacuum conditions which were necessary in the preparation of thin films. Moreover, the critical dependence of the film properties on various deposition conditions makes the exact reproducibility of deposition conditions absolutely imperative for consistency in results. In earlier stages of thin-film studies, no concord existed in the data collected in different experiments. In the last two decades, however, there has been an appreciable improvement in vacuum technology. Partly because of this and partly due to the advent of sophisticated electron-optical methods for characterization of the deposited films, study of thin films has made significant progress. Because of their indispensability in integrated circuits and microelectronics, thin films caught the interest of many researchers. However, there is still no universally consistent picture, and the present day research is centered on efforts to understand better the phenomena in these systems.

The major techniques for structural studies of thin films are electron microscopy and x-ray, electron, and neutron diffraction. While electron microscopy [1] gives a qualitative description of the system, electron and x-ray diffractions give an overall idea of the lattice constants. Electron and x-ray diffractions, though accurate in their quantitative estimate of crystallographic structure in films, fail to give any idea regarding the degree of covalency of bonds, the coordination number, phonon frequencies, and the degree of order in films. Optical methods lack the resolution to provide direct data on the crystallographic structure of thin films. These methods are useful only in supplementing information on the correlation of deposition parameters, composition, structure, and microphysical properties. Radial distribution function (RDF) studies [2] sometimes lead to ambiguous information regarding

coordination number. It is observed that sometimes more than one value of the coordination number fit in with RDF data.

It is obvious that the methods previously mentioned are not adequate to study thin films. A need exists to explore the possibilities of studying these systems by as many other methods as possible. The Mössbauer effect is one of the important tools for any kind of structural studies, and this has not been fully exploited in the field of thin films. Although some Mössbauer studies have been made in thin films, they lack a systematic approach and coherence.

Lee et al. [3] made the first Mössbauer spectroscopic studies on magnetic thin films of iron having thicknesses from a few hundred angstroms to a few thousand angstroms. They observed a six-line pattern down to 5 Å thickness and below this thickness the onset of superparamagnetic relaxation was seen. Zuppero and Hoffman [4] improved upon the work of Lee et al. by using ultrahigh vacuum conditions to minimize oxidation of iron films during their formation. They found that the value of internal field for 1000 Å thick film was 20 percent less than the value for bulk samples. Verma and Hoffman [5], on studying the samples in ultrahigh vacuum, found that the six-line pattern for films with thickness as low as 10 Å has internal field only 3 to 4 percent less than bulk value. For lower thicknesses, they observed a doublet with very large quadrupole splitting. Evidence of superparamagnetic fluctuations was also observed. Recently, Boorchard et al. [6] have made a study of amorphous $\text{Ge}_{1-x}\text{Te}_x$ alloy films using the Mössbauer technique and have illustrated the advantages of this technique. However, the interpretation given by the authors regarding the coordination in these systems is in contradiction with the electrical, optical, and RDF studies made on these systems.

Theoretical aspects of the Mössbauer effect in thin films have been considered by Corciovei et al. [7] and Valenta et al. [8]. Corciovei et al. studied the thermal vibrations in a cubic thin film in the harmonic first neighbor approximation and pointed out the appearance of anisotropy in the Debye-Waller factor with respect to the angle between the normal to the film surface and the direction of emitted and absorbed gamma-quanta. They also predicted a decrease in the Mössbauer fraction with decreasing film thickness. They suggested the possibility of the appearance of Goldanskii-Kraygin effect in noncubic thin films. Valenta et al. considered the problem of spatial distribution of spontaneous magnetization in thin films using molecular field approximation and Green function technique. Since, in the absence of relaxation effects, the spontaneous

magnetization and the internal field are very nearly proportional to each other, Mössbauer spectroscopy can be used to study these predictions.

In light of the earlier work, the present work was initiated with the aim of studying the variation of Mössbauer parameters with film thickness so as to derive information about the nature of bonds and the film structure. To understand thin films better, bulk FeTe was also studied.

Bulk FeTe systems have been studied extensively by many researchers Suwalski et al. [9] studied $\text{Fe}_{1.11}\text{Te}$ and fitted a single quadrupole doublet to the data. Fano and Ortalli [10] fitted two quadrupole doublets to their data on $\text{FeTe}_{0.95}$ and explained them as being due to two nonequivalent sites of iron. The interpretations given by these two groups of researchers do not agree; these disagreements cannot be attributed to the small stoichiometric difference in the two systems. Albanese et al. [11] studied FeTe using Te^{125} isotope and observed a quadrupole doublet. They attributed the asymmetry in the lines to preferential orientation of monocrystals.

II. EXPERIMENTAL DETAILS

The details of various stages of the experimentation are presented as follows.

A. Sample Preparation and Characterization

1. Bulk. X-ray powder diffraction patterns of commercially available FeTe were taken using a Philips x-ray machine with iron as the target. The machine was operated at 30 kV — 13 amp. Figure 1 shows the observed x-ray photograph. The d-values were measured using a comparator. The good agreement of the observed d-values with standard values provided a check for the single phase nature of the starting materials.

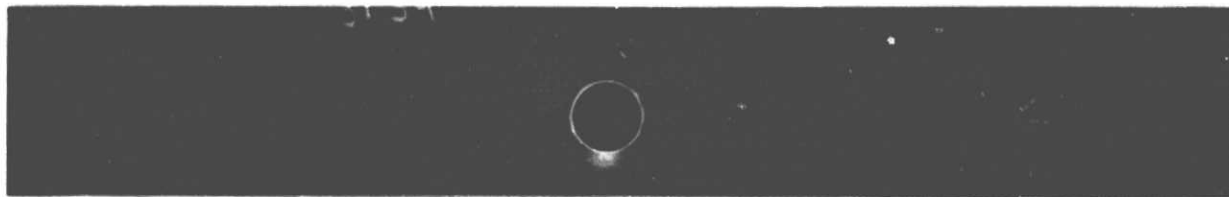


Figure 1. Photograph of x-ray diffraction pattern of bulk FeTe.

2. Thin Films. After characterization of the starting bulks, thin films of these materials were deposited. A flash evaporation method was used for deposition because the constituents forming the compound differ greatly in their vapor pressures. In such cases, the films deposited by the simple thermal evaporation method, in which the starting material (in form a mixture or compound of the constituents) is placed in the a boat and heated electrically, are likely to have compositions quite different from those of the starting materials; the more volatile of the constituents tend to have a higher concentration in the films. For such cases, two often-used modified thermal evaporation methods [12] are (a) two-source method and (b) flash evaporation method. In the two-source method, each constituent is evaporated in a separate boat. This method requires that the vapor density of the constituents and the temperatures of the two boats be adjusted critically. Being dependent on many factors, this method involves difficulties and does not give the exact compositional ratio. With reactive metals such as iron as one of the constituents, the two-source method becomes even less practicable. In the alternative method of flash evaporation, fine particles of the material are dropped onto a boat heated to a temperature higher than the temperature required to evaporate all the constituents so that the particles get evaporated as soon as they touch the hot boat surface. The flash evaporation method for film deposition was chosen because this method involves fewer adjustments. The vapor density and temperature of the boat do not need to be monitored, the only requirement being that the hot surface be maintained at a temperature higher than is required to evaporate the less volatile constituent. A good control of film composition is achieved in this method.

To provide a steady trickle of the evaporants, a powder dispenser which operated electromagnetically was used. The electromagnet is controlled from outside the vacuum chamber and can be adjusted to drop the evaporant onto the heated boat at the required rate. With one of the constituents being iron in all the cases, the boat was required to withstand temperatures on the order of 2000°C without volatilization. Strips of tantalum bent into boats deep enough to avoid waste of material (because of particle ejection) were used as heating sources. The pressure was maintained at 10^{-6} torr. Degassing in the system was reduced by initially heating the filament to a very high temperature. The substrate was kept at a distance of approximately 25 cm from the boat. Provision was made for another boat so as to deposit layers of SiO in between two consecutive films of the material. This was done to insulate the films from one another. Stacking of films was necessary to provide enough total iron content to be detected by the Mössbauer technique.

The thickness of the films was monitored using a quartz crystal thickness monitor [13]. In a monitor of this kind, an oscillating quartz (6.0 MHz/s) crystal is positioned inside, and another one (6.5 MHz/s) is positioned outside the coating chamber. As deposition proceeds, the frequency of the crystal in the coating chamber changes as a result of the evaporant deposited on it. Measurements are taken of the frequency differences between the two crystals. This is done by first amplifying this difference signal and feeding it into a unit where it is mixed with a variable oscillator to produce a final difference frequency. Repeatability for the same set of chamber conditions is usually good. In practice, the accuracy of crystal oscillator monitors is determined by the stability of the oscillator circuit.

For the purpose of characterization, some of the films were deposited on freshly cleaned NaCl single crystal slices. These were studied using electron transmission and diffraction photographs, some of which are given in Figure 2. Within the limitations of measurements made on the electron microscope, the d-lines obtained from these sets of diffraction patterns using a densitometer compared well with the values for bulk.



Figure 2. Transmission electron diffraction pattern of thin film of FeTe (500 Å thickness).

3. Mössbauer Spectrometer. The samples were in turn mounted on a Mössbauer spectrometer for further study. The Mössbauer spectrometer consisted of a 400 multichannel analyzer incorporated with a constant acceleration

electromagnetic drive. The gamma rays are detected by a 1 mm thick NaI scintillation crystal coupled to a Harshaw Photomultiplier tube No. K9685, CW352. The source and detector were arranged so that the solid angle at the source, made by the gamma rays reaching the detector, was approximately 0.12 rad. A thin beryllium window in front of the NaI crystal was used to cut off 6.3 keV x-rays from the Co^{57} source. The single channel unit is an energy selective unit and was set to detect 14.4 keV gamma rays from the Co^{57} source in Pd matrix. The data output was taken onto a teletype unit provided with a typewriter that records the number of pulses stored in each channel of the memory.

Calibration spectra were taken using a 310 alloy stainless steel foil and sodium nitroprusside powder. The Mössbauer spectra were analyzed with the help of an ICL 1900 computer. After making a rough visual estimate of the number of lines and the different Mössbauer parameters, the data were fed to the computer to get the best fit of Lorentzian curves within the constraints of a specified convergence criterion [14].

The stability of the instrument was checked by taking a number of spectra for the standard absorbers and comparing the computer-fit parameters obtained in the different runs. These spectra were repeated after regular intervals to provide a check on the stability of the instrument.

B. Results and Discussion

1. Bulk — FeTe. The computer fit spectrum of bulk FeTe (Fig. 3) shows the presence of two lines: one at (0.428 ± 0.022) mm/s and the other at (0.01 ± 0.013) mm/s. FeTe bond is highly covalent (93 percent covalency from electronegativity considerations). It is known that in low spin, highly covalent complexes isomer shift (IS) values for Fe^{2+} and Fe^{3+} state are almost equal [15]. Since in the present study the two lines are far apart it is concluded that they belong to a quadrupole doublet and not to two-charge states of iron. There is only one noncubic iron site corresponding to the hexagonal structure [16] that FeTe is known to have.

The observed IS value of 0.224 ± 0.022 mm/s suggests a highly covalent $3d^2 4s 4p^3$ hybridized state of Fe^{2+} ion and gives a 66 percent 4s electron configuration according to the Jaccarino-Walker diagram [17]. Taking the hybridization into account, this implies an almost 100 percent covalency which agrees well with the electronegativity difference of Fe and Te.

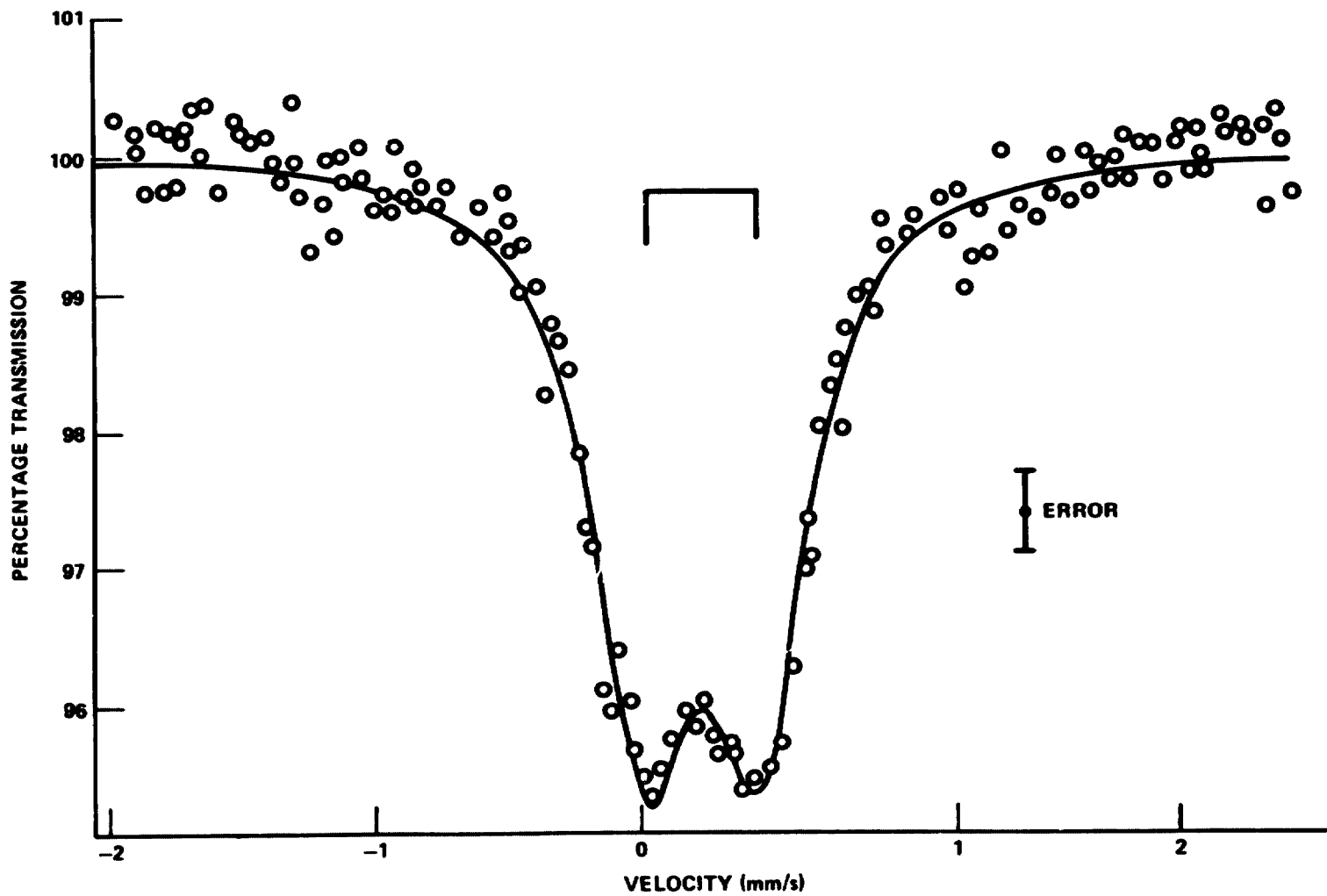


Figure 3. Mössbauer spectrum of bulk FeTe.

The quadrupole splitting (QS) value of the observed doublet is (0.428 ± 0.022) mm/s. Treating the Te and Fe sites as equivalent in the hexagonal NiAs structure of FeTe, the Earth's field of gravitation (EFG) at the two sites can be said to be the same except for the much larger values of antishielding factor for Te. Taking this factor and the value of quadrupole moment for Te into account, the QS value observed by us agrees with Albanese et al.'s work. As previously mentioned, Suwalski et al. on the basis of their study of Zeeman's splitting pattern of $\text{Fe}_{1.11}\text{Te}$ concluded that in this system the main EFG contribution is from the ligands alone, the valence contribution being negligible. Since in the sample being investigated in the present study the nature of bond is very similar, it is concluded that valence contribution to EFG in FeTe is negligible. To verify this conclusion, calculations were made to find an estimate of the ligand contribution to EFG to determine how they compare with the experimental values. The point charge model was used in these calculations. Strictly speaking, this model applies to ionic cases only; however, it gives a reliable estimate in the presence of covalent bonds also if adequate corrections for the covalency are made.

The EFG thus calculated work out to be $V_{zz} = -11.3 \times 10^{20}$ V/m². This gives the value 0.422 mm/s for Q value of 0.36b. The good agreement of this calculation with the experimental value indicates that the main EFG contribution comes from the lattice, the valence contribution being negligible.

In summary, the Mössbauer spectrum of bulk FeTe shows a quadrupole doublet whose splitting agrees with the ligand calculations made using the hexagonal structure for FeTe, proving that the contribution to EFG from valence electrons is negligible. The charge state is low spin Fe^{2+} with a strongly covalent $3d^2 4s 4p^3$ hybridized bond.

2. Thin Films of FeTe on Amorphous Substrate. Figures 4 through 8 show the Mössbauer spectra of films of various thicknesses (80 Å, 180 Å, 730 Å, 2000 Å, and 4000 Å) deposited on mylar substrate. Each spectrum shows the existence of two distinct well resolved lines. Because the widths of these lines were much larger than those for the standard samples, the authors were prompted to attempt fitting more than two lines. The computer, however, gave the best fit only for two lines.

As explained in Reference [18], the structure of thin films is essentially the same as that of their bulk unless there is a drastic change either in the coordination number or in the basic crystal structure. The electron diffraction

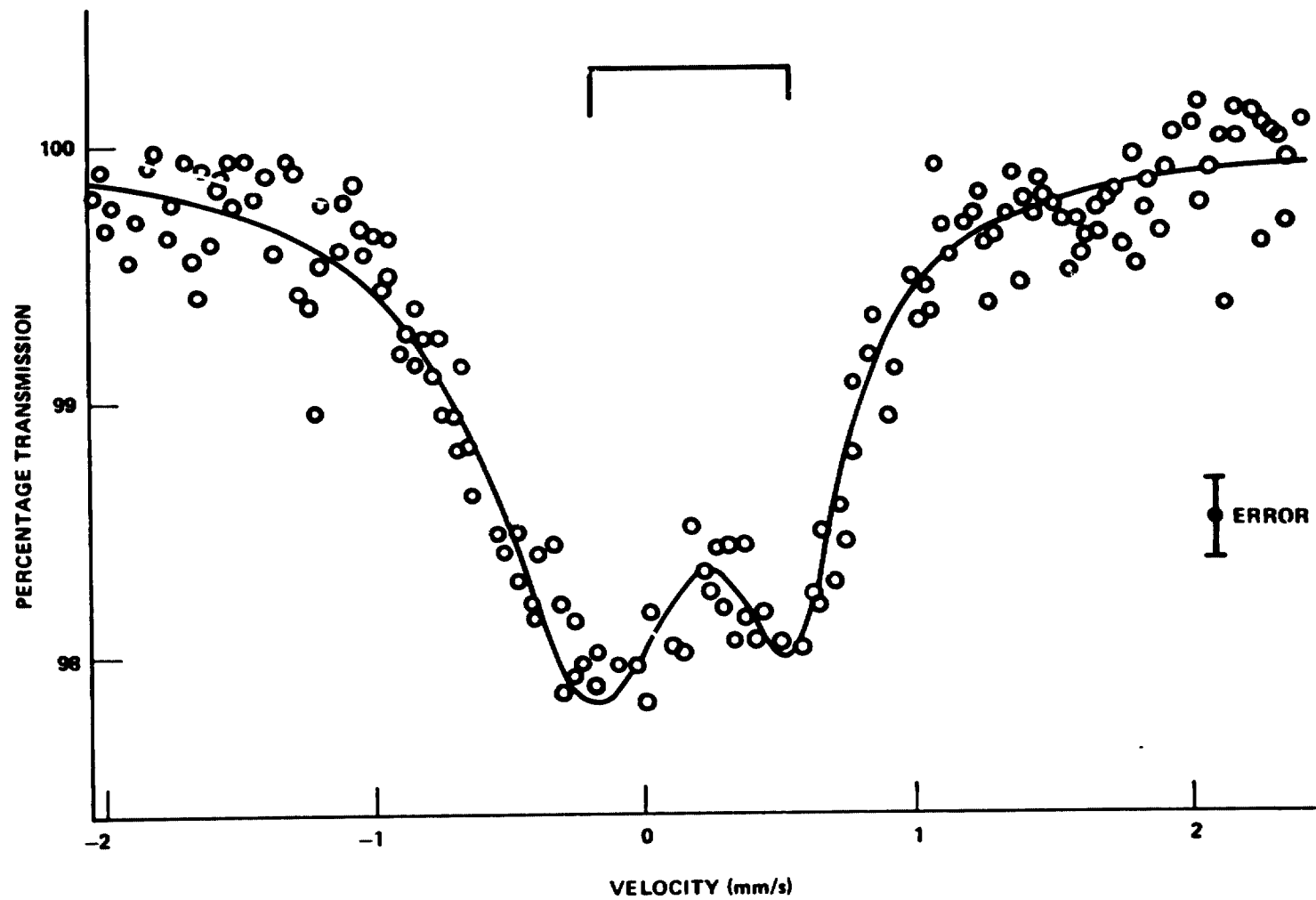


Figure 4. Mössbauer spectrum of FeTe film 80 Å (freshly deposited).

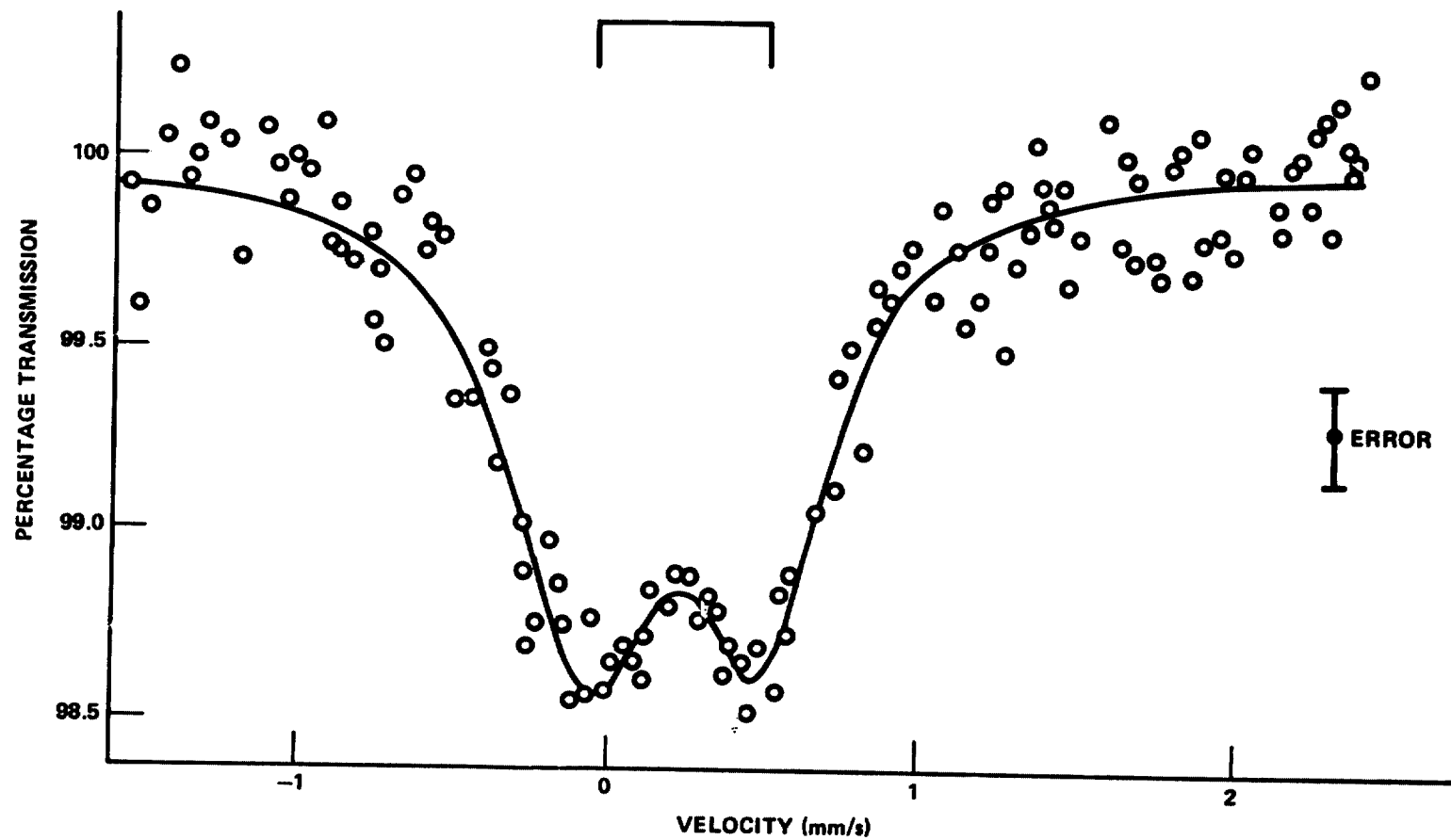


Figure 5. Mössbauer spectrum of FeTe film 180 Å (freshly deposited).

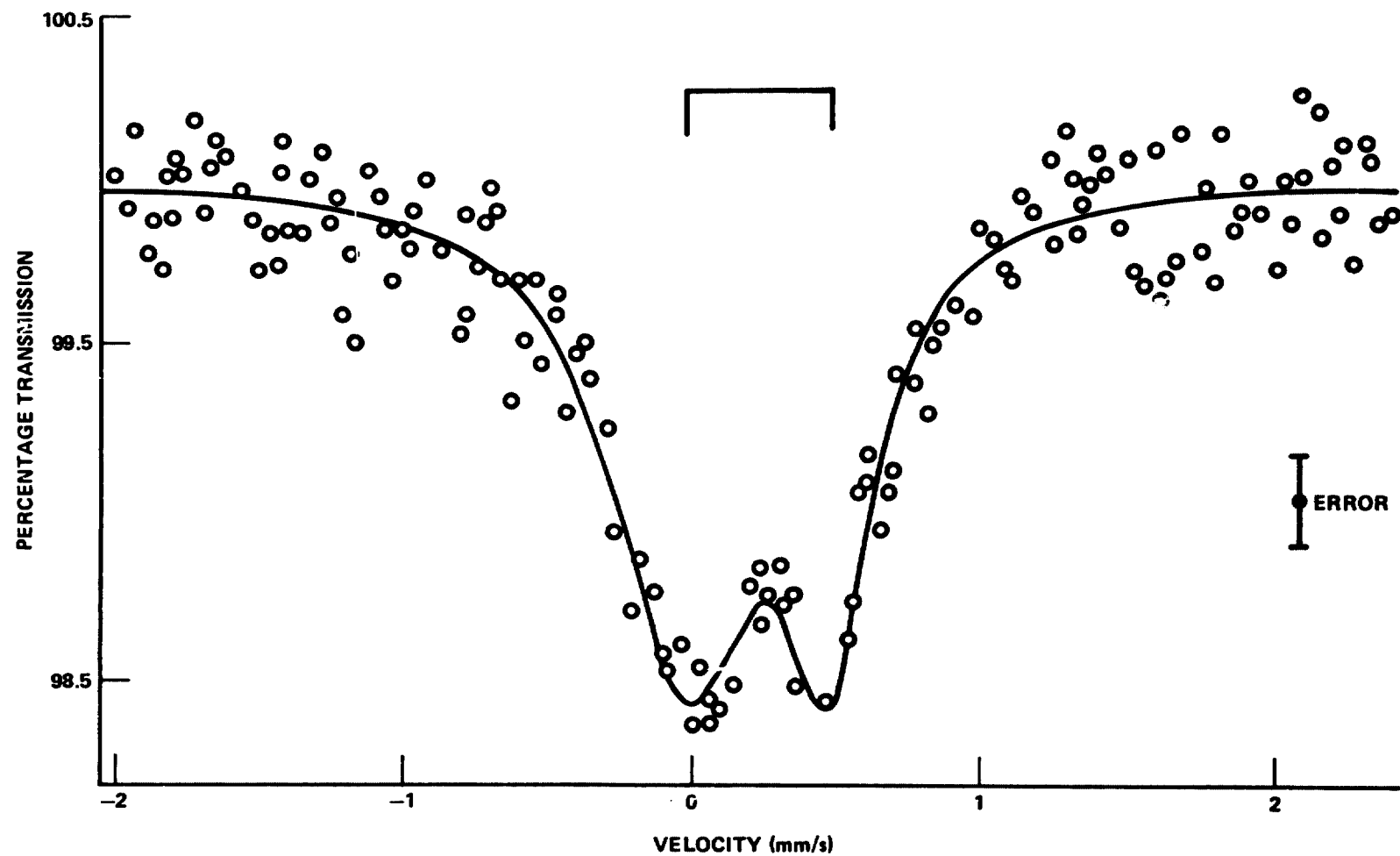


Figure 6. Mössbauer spectrum of FeTe film 730 Å (freshly deposited).

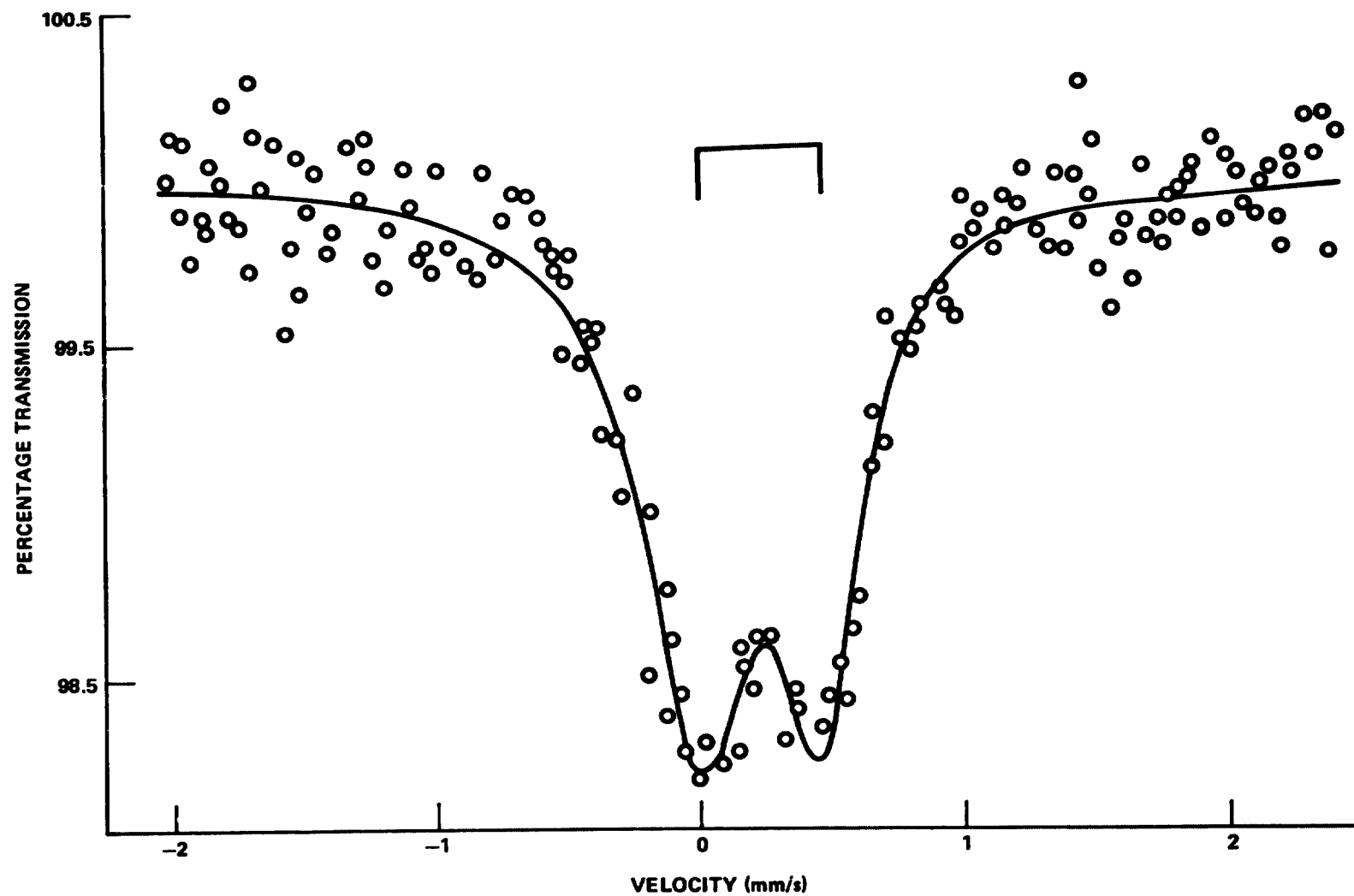


Figure 7. Mössbauer spectrum of FeTe film 2000 Å (freshly deposited).

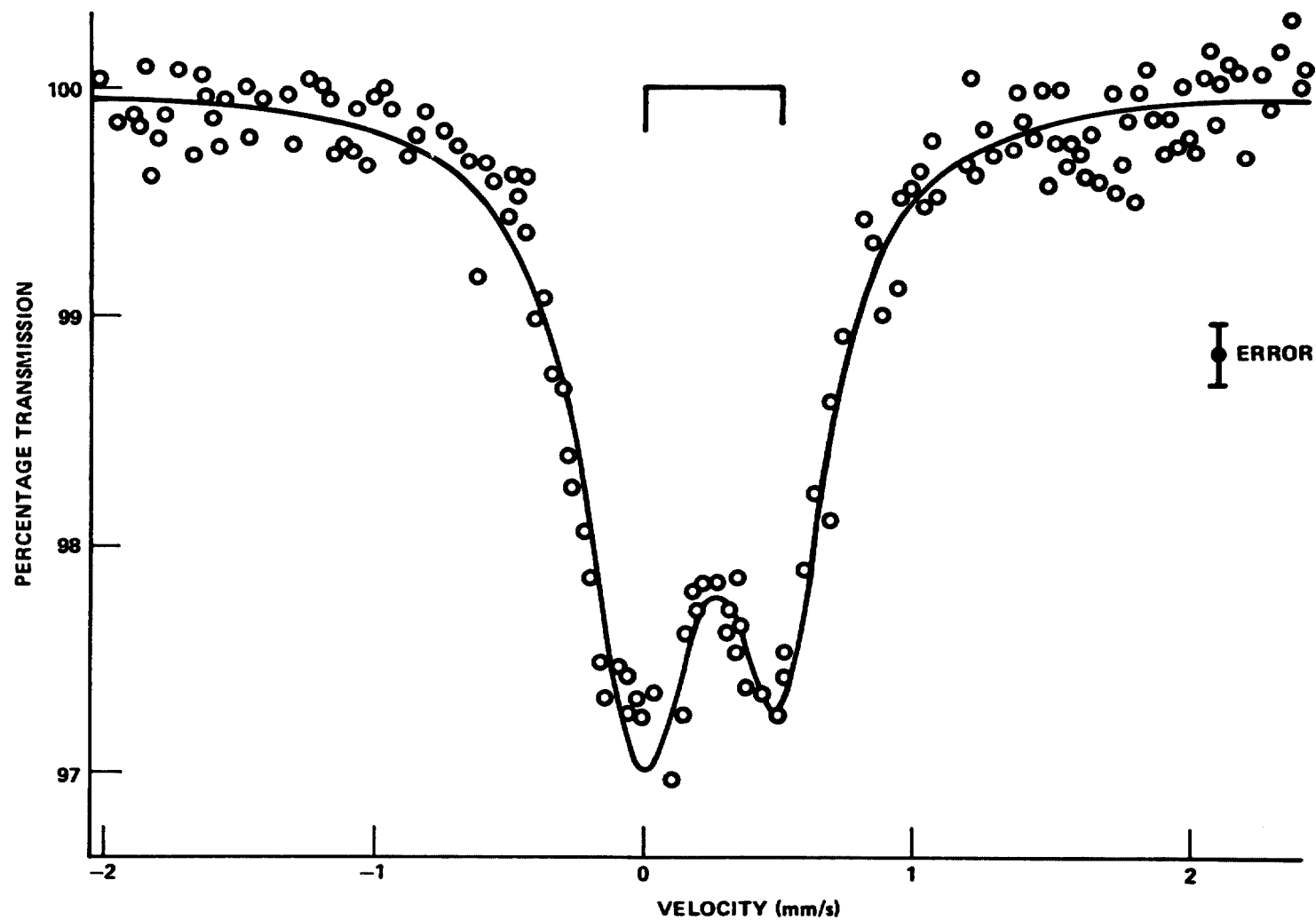


Figure 8. Mössbauer spectrum of FeTe 4000 Å (freshly deposited).

study did not indicate any such changes. It was therefore reasonable to expect that the two lines observed in the Mössbauer spectra of thin films corresponded to a quadrupole doublet of a noncubic iron site. The Table gives the Mössbauer parameters for the quadrupole doublets observed in different films.

In Figure 9, which gives the variations of IS and QS values with film thickness, it can be seen that IS values are the same for thicknesses down to 1000 Å. Below 1000 Å, there is a decrease in the IS values with decrease in film thickness. This observed variation implies an increase in s-electron density at the iron site with decrease in film thickness for thicknesses below 1000 Å. As previously discussed, FeTe is a highly covalent compound having an octahedral symmetry. Iron is in the $\text{Fe}^{2+} 3d^2 4s 4p^3$ hybridized state. The two empty d-orbitals of Fe^{2+} together with one 4s and three 4p empty orbitals participate in the formation of six covalent bonds with the ligands. Each hybridized orbital is occupied by the electrons which are shared by the corresponding two ions. If one of the bonds is broken, the electrons distributed in the $3d^2 4s 4p^3$ hybridized shells partly come back to the two 4s shells corresponding to the $3d^6 4s^2$ structure of iron. Breaking of one of the bonds therefore leads to an increase in the s-electron density at the nucleus and hence a decrease in the IS value. The decrease in the IS values observed at lower thicknesses thus indicates unsatisfied bond structure having some missing bonds (also referred to as dangling bonds). The existence of dangling bonds has been indicated earlier on the basis of conductivity measurements in some thin films [19]. If the substrate is kept at room temperature, the deposited ions have low mobility, and in the initial stages of film growth they tend to stick to the substrate randomly wherever they impinge on it. The probability of bond formation between the ions is small because of the sluggish motion of ions, and this leads to unsatisfied bonds and incomplete crystal structures in the films. As the deposition process continues, some of the ions reaching the substrate fill the gaps left in the initial stages of film formation and complete some of the missing bonds. As a result, there are less number of dangling bonds at higher thicknesses and a higher IS value is seen. Furthermore, the near uniform IS value for films with thicknesses at approximately 1000 Å and above being equal to the value for bulk suggests that the change in the dangling bond density beyond 1000 Å is very small. This limit of 1000 Å thickness is an approximate estimate because the observations were taken at discrete values of thickness. It would be of interest and benefit if similar IS variation studies were made on films deposited on substrates kept at higher temperatures. This study would reveal how substrate temperature influences the critical thickness above which the film behaves like bulk where the

TABLE. MÖSSBAUER PARAMETERS OBSERVED IN FeTe SYSTEM (FRESHLY
DEPOSITED FILMS ON AMORPHOUS SUBSTRATES)

Thickness (Å)	IS (mm/s)	QS (mm/s)	W_1/W_2	W_1 (mm/s)	A_1/A_2
80	0.17 ± 0.023	0.738 ± 0.028	1.98 ± 0.4	0.994 ± 0.040	2.92 ± 0.29
130	0.214 ± 0.024	0.562 ± 0.028	1.23 ± 0.2	0.616 ± 0.034	1.39 ± 0.17
730	0.229 ± 0.018	0.500 ± 0.023	1.62 ± 0.3	0.611 ± 0.027	1.90 ± 0.19
2000	0.234 ± 0.016	0.468 ± 0.022	1.49 ± 0.2	0.535 ± 0.020	1.75 ± 0.16
4000	0.24 ± 0.014	0.50 ± 0.019	1.3 ± 0.18	0.526 ± 0.016	1.62 ± 0.11
Bulk	0.224 ± 0.018	0.428 ± 0.022	1.04 ± 0.2	0.454 ± 0.020	1.0 ± 0.10

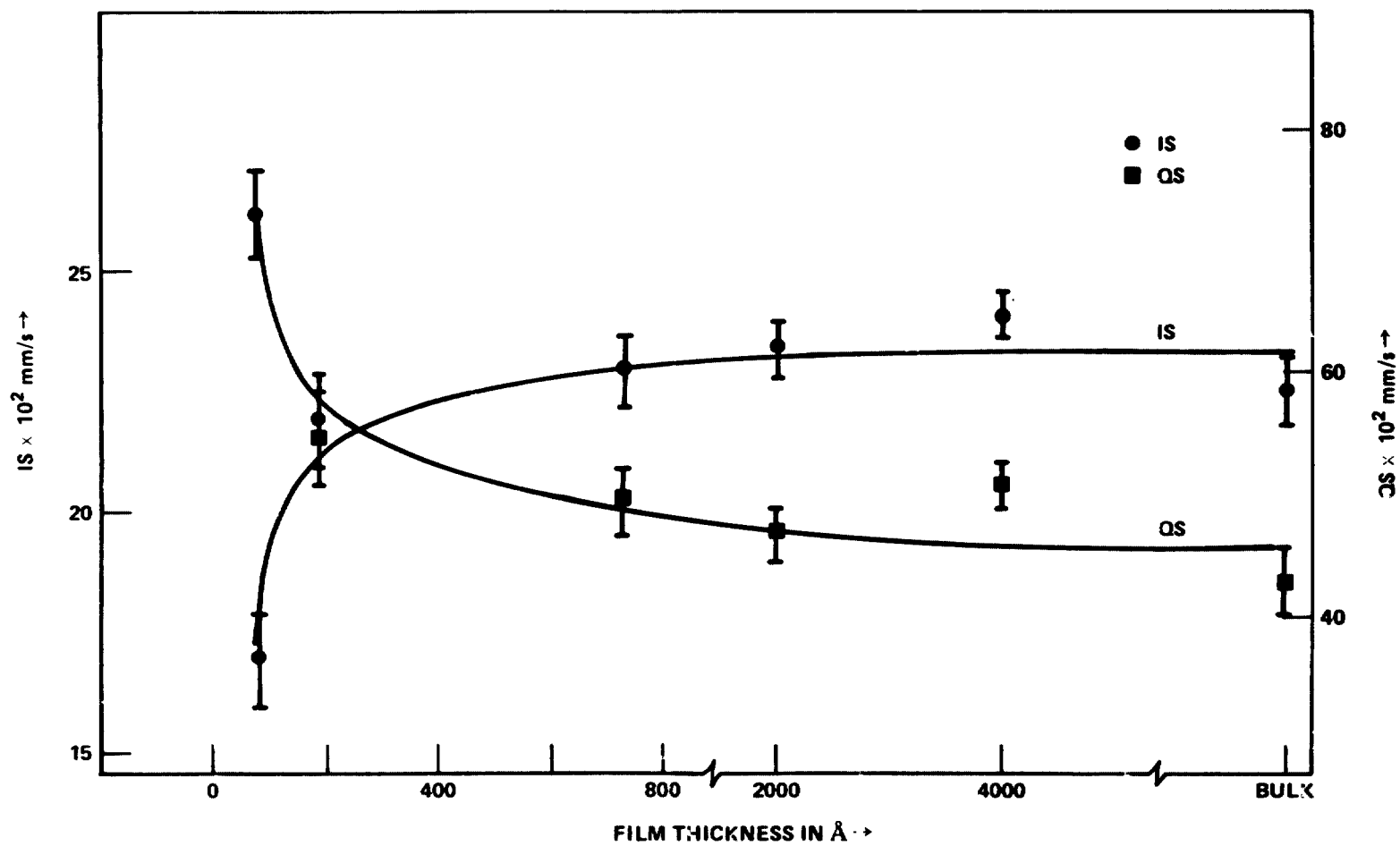


Figure 9. Variations of IS and QS values with film thickness.

presence of dangling bonds is concerned. Such studies will also provide a check on the explanation of IS behavior previously given, the value of the critical thickness above which the film would behave like a bulk should be lower for substrates at higher temperatures.

The QS values for different thicknesses recorded in the Table are shown in Figure 9. The observed variation indicates a greater degree of crystal distortion from cubic symmetry at lower thicknesses. An increase in the ionic character of bonds could result in an increase in the QS values. Such an increase would simultaneously result in an increase in IS value for the Fe^{2+} ion. Since in the present study an opposite behavior of IS variation with thickness (i.e. a decrease in IS with a decrease in thickness) has been observed, the increase in the QS values at lower thicknesses cannot be due to an increase in the ionic character of the bonds. The observed QS can be understood only on the basis of a larger distortion from cubic symmetry in films of lower thicknesses. This suggests the existence of incomplete crystal structures at low thicknesses. The crystal symmetry at any point in the lattice is lowered if some of the bonds existing in its immediate neighborhood disappear or are unsatisfied. This gives rise to a higher gradient of electric field at that point. It can be seen in Figure 9 that the QS values for thicknesses greater than 1000 Å are almost constant and equal to the bulk QS value. This indicates that for thicknesses above 1000 Å, the crystal symmetry in the films is identical to the bulk. This observation is in agreement with similar conclusions drawn on the basis of IS considerations previously mentioned.

As previously discussed, most of the Mössbauer lines for FeTe thin films have widths larger than the widths of lines corresponding to standard absorbers and those of the lines corresponding to the bulk, the first line being broader than the second. The thickness variation of line width asymmetry (W_1/W_2) of the doublets is shown in Figure 10 and indicates a reduction in the asymmetry with increase in thickness.

In general, line broadening in Mössbauer spectra suggests the presence of relaxation effects and/or structural disorder. Relaxation basically implies that during the time of nuclear transition some changes in the system take place which are only partially resolved. That the relaxation processes, both of magnetic and thermal origin, are not present in the system under study follows from the facts that:

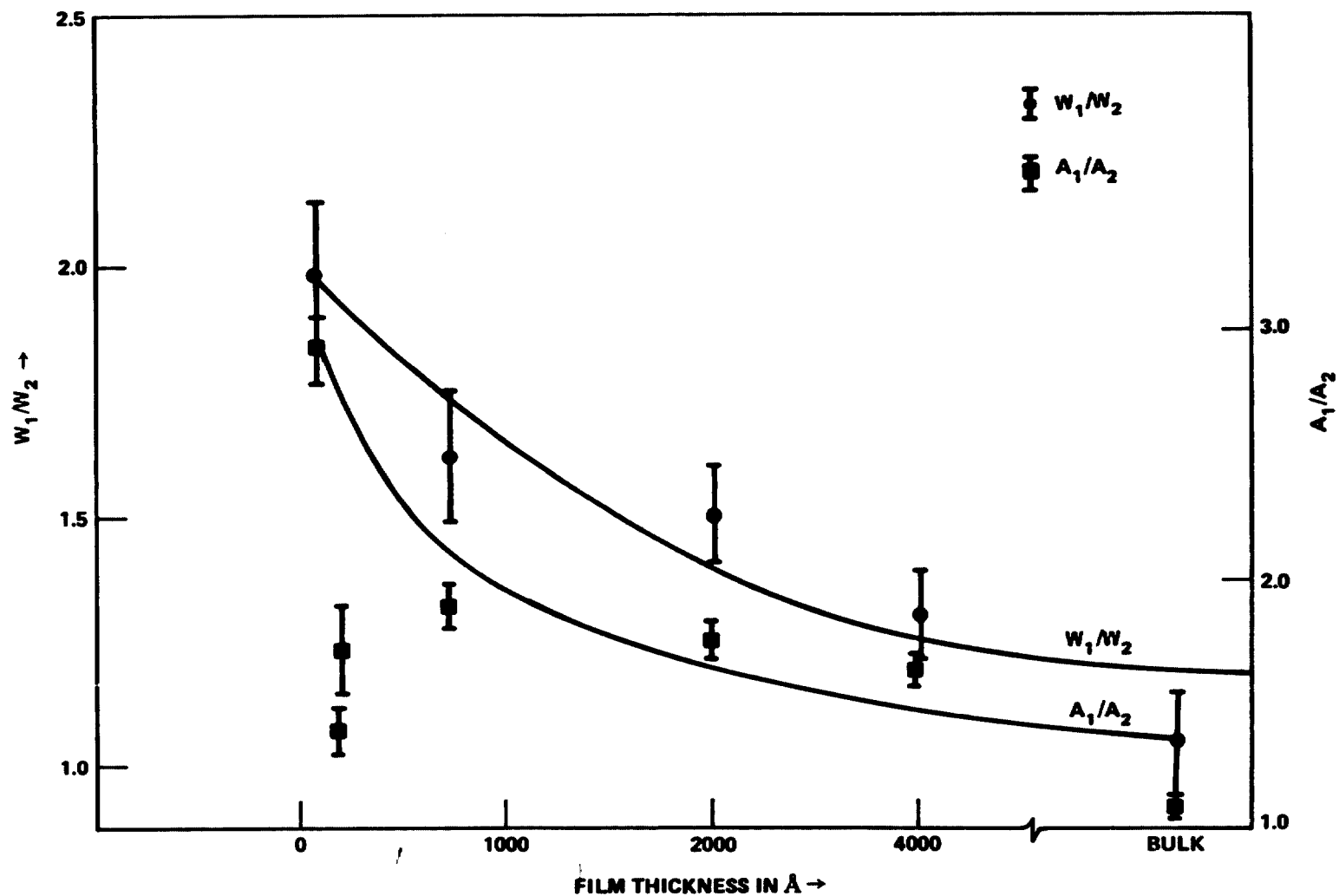


Figure 10. Thickness variation of line width asymmetry of the doublets.

a. Since the corresponding spectra were taken at the same temperature (room temperature), the spin-lattice interaction which is temperature dependent cannot be different in the bulk and thin films.

b. Since there was no diamagnetic dilution of the sample in thin films, spin-spin interactions in the bulk and films are the same.

c. As previously discussed, the nature of QS and IS variations with film thickness indicated an absence of changes in the nature of the bonds and hence bond lengths (this means that the FeTe distance could not have changed and is supported by the x-ray and electron diffraction studies of the bulk and thin films, respectively).

d. Since the study was confined to room temperature only, thermal relaxation which occurs near melting point of material could not be present.

The other possible reason for the broadening of a Mössbauer line is the presence of structural disorder. Presence of structural disorder could lead to variations in QS and/or IS values within the sample; in case only one of the parameters shows a scatter in its values, the two components of a quadrupole doublet will experience equal broadening. However, if both QS and IS values vary simultaneously, the lines of the doublet may show an asymmetry in width. Preston et al. [20] have explained the line width asymmetry observed in spectra of some disordered alloys on the basis of simultaneous existence of IS and QS variations. A film of a particular thickness would show a certain variation in the dangling bond configuration at the various iron sites, resulting in different IS and QS values for these sites. Furthermore, since the presence of dangling bonds affects the QS and IS parameters in opposite fashion, the bond configuration that leads to a higher QS value corresponds to a lower IS value. The correlation between the QS and IS variation leads to the observed width asymmetry.

It is apparent from the previous discussion that the width of the first line (W_1) is a measure of the degree of disorder in the film. Figure 11 indicates that the films exhibit lower disorders at higher thicknesses. This is in concurrence with the QS and IS variation with film thickness on the basis of which it has been deduced that for higher film thickness the dangling bond density decreases.

The areas under the two components of the quadrupole doublet were found to be unequal. The variation of ratio of the areas with film thickness, i.e. the area asymmetry, is shown in Figure 10. It is seen that the asymmetry is smaller at higher thicknesses. Asymmetry of areas under the components of a quadrupole doublet indicates either the presence of the Goldanskii-Karyagin effect or a certain

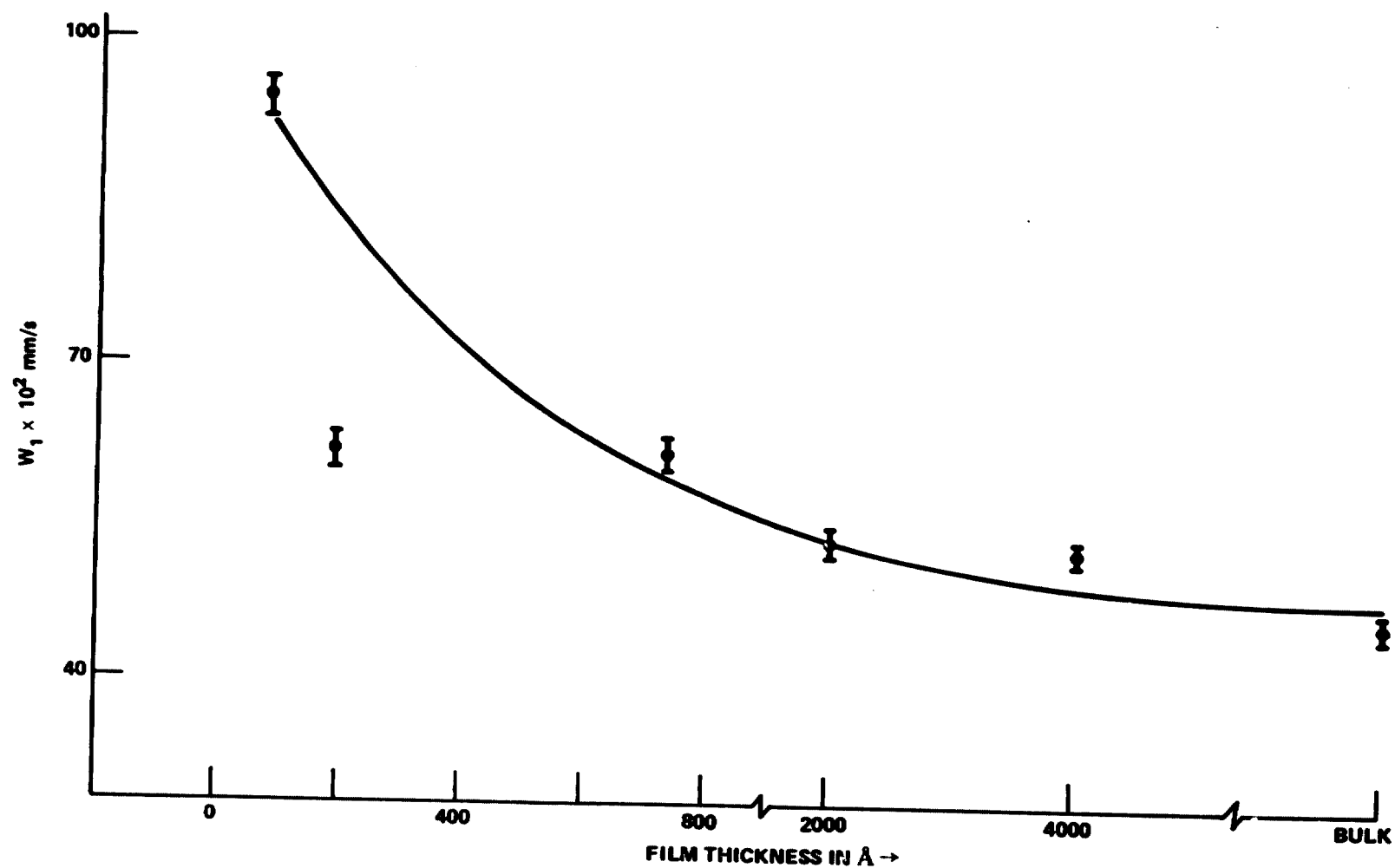


Figure 11. Variation of W_1 with film thickness.

degree of preferential orientation of the monocrystals in the material. The second kind of asymmetry would depend on the angle that the axis of preferential orientation makes with the gamma ray direction.

In the present study it was observed that for all film thicknesses the magnitude of asymmetry was too large to be due to the Goldanskii effect alone. This suggested the presence of a degree of preferential orientation of the crystallites in the films studied. The existence of oriented growth or fiber structure in films at all stages of film growth (during nucleation, coalescence etc.) and for all conditions of growth (exptaxial growth, oblique growth, annealing etc.) has been reported [21]. On amorphous substrates, existence of fiber texture has been reported mostly for low film thicknesses [21]. This tendency is more pronounced in case of hexagonal close packed (HCP) structure. Since in the present experiment the same deposition conditions were maintained for all film thicknesses, the direction of texture formation in all films is expected to be the same, the structure of the sample being HCP. The uniform decrease in the area asymmetry with increasing film thickness indicates a lesser degree of orientation at higher film thicknesses. Maximum area asymmetry is observed at 80 Å film thickness. At this thickness, the film is in the form of islands; the islands are scattered on the substrate in the form of unconnected bunches and these bunches are highly oriented. A similar oriented structure at low thicknesses was observed by Wade and Silcox [22] using small angle electron scattering experiments for Pd, Ni, and permalloy films. A decrease was observed in the area asymmetry as film thickness was increased. This indicates that during the coalescence of the islands, the initial orientation is partly disturbed leading to smaller area asymmetry. To form a rough idea of the variation of the area asymmetry with the relative angle between the gamma ray direction and the axis of orientation, the film with a 4000 Å thickness was studied at an inclination of 45°. A 33 percent change in A_1/A_2 value was observed. The definite dependence of A_1/A_2 on the angle supports the argument that the area asymmetry observed is a consequence of oriented fiber texture. However, to give a qualitative estimate of the orientation, a more detailed Mössbauer study of all the films by varying the angle of orientation is needed.

3. Substrate Influence. To see the effect of substrate on film structure, films of 500 Å and 1000 Å thicknesses were deposited on aluminum substrate (Figs. 12 and 13). The Mössbauer spectra of these films were found to be very different from the ones deposited on mylar sheet. The lines are slightly broadened but could not be split into two which indicates the absence of any appreciable EFG at the iron site. The film structure is therefore near cubic which is quite

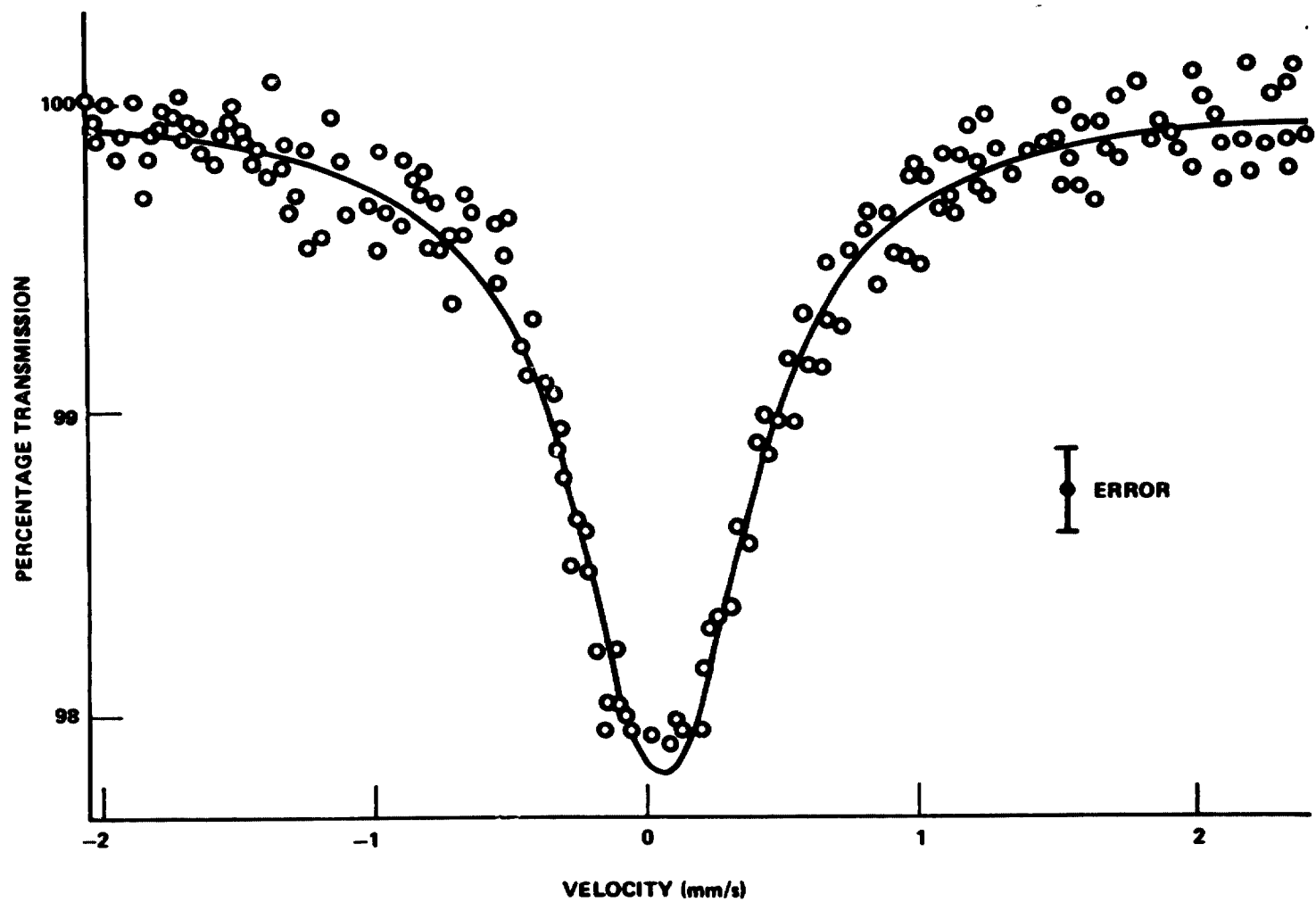


Figure 12. Mössbauer spectrum of FeTe film 500 Å (deposited on aluminum substrate).

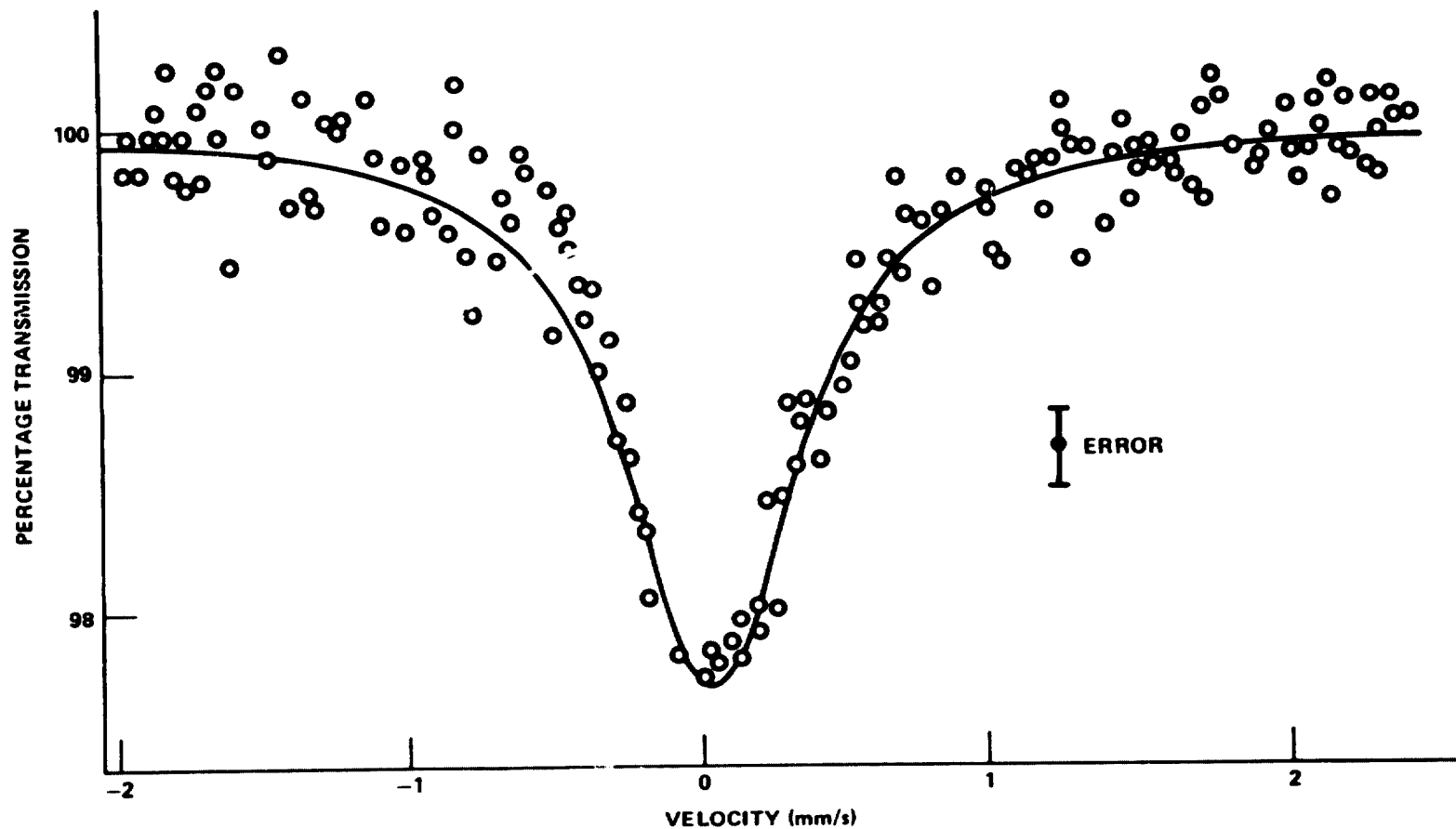


Figure 13. Mössbauer spectrum of FeTe film 1000 Å (deposited on aluminum substrate).

unlike the bulk as well as the films deposited on amorphous substrate. This reflects on the influence of the crystal structure of aluminum substrate on the structure of the deposited film. The cubic face center cubic (FCC) structure of the substrate dominates over the initial HCP noncubic structure of the starting material and is maintained even for thicknesses as high as 1000 Å. In this case, it is not a very surprising observation because the HCP structure is quite similar to the FCC structure and crystal transformations similar to the one observed here are not uncommon in the literature [23]. It is interesting to note that the IS values of these films are very different from those of films deposited on amorphous substrate. This indicates that not only the crystal structure but the nature of the bonds also get modified.

In summary, it is observed that FeTe has only one noncubic Fe^{2+} site which is $3d^2 4s 4p^3$ hybridized. Thin films of FeTe, although similar in structure to the bulk, show the presence of dangling bonds. The films show a tendency of preferential orientation; this tendency decreases with increasing film thickness. The substrate influences the film structure and the nature of bonds in films.

REFERENCES

1. Pinsker, Z. G.: Electron Diffraction. Butterworths London, 1953.
2. Adler, D.: Amorphous Semiconductors. Butterworths London, 1971.
3. Lee, F. L., Boldue, P. L., and Violet, C. E.: Phys. Rev. Lett., vol. 13, 1964, p. 800.
4. Zuppero, A. C. and Hoffman, R. W.: J. Vac. Science and Technology, vol. 7, 1970, p. 118.
5. Verma, M. N. and Hoffman, R. W.: J. Appl. Phys., vol. 42, 1971, p. 1727.
6. Boolchand, P., Triplett, B. B., Hanna, S. S., and de Neufville, J. P.: Mössbauer Effect Methodology. Plenum Press, New York and London, 1974.
7. Corciovei, A., Green, D., and Radescue, E.: Z. Physik, vol. 209, 1968, p. 134.
8. Valenta, L., Haubenreisser, W., and Brodkorv, W.: Phys. Stat. Sol., vol. 26, 1968, p. 191.
9. Suwalskii, J., Piekoszewski, J., and Leciejewicz, J.: Proceedings of the Conference on the Application of Mössbauer Effect (Tihany), 1969.
10. Fano, V., Ortalli, I.: Proceedings of the IV International Conference on Mössbauer Spectrometry (Dresden), 1971.
11. Albanese, G., Lamborizio, C., and Ortalli, I.: Il. Nuovo Cimento Serie X, vol. 50, 1967, p. 65.
12. Handbook of Thin Film Technology. Maissel, L. I. and Glang, R. (eds.), McGraw-Hill Book Company, 1970.
13. Riegert, R. P.: Proc. 4th Intern. Vacuum Congress, The Institute of Physics and Physical Soc., 1968.

REFERENCES (Concluded)

14. Gupta, R. G.: Mössbauer Studies in Mn-Zn Ferrites. Ph.D. Thesis, I. I. T. Delhi, 1975.
15. Shulman, R. G., and Sugano, S.: J. Chem. Phys., vol. 42, 1965, p. 39.
16. Oftedal, I.: Z. Physik. Chem., vol. 132, 1928, p. 208.

Wychoff, R. W. G.: Crystal Structure: Interscience Publishers, Inc., New York.
17. Walker, L. R., Wertheim, G. K., and Jaccarino, V.: Phys. Rev. Lett., vol. 6, 1961, p. 98.
18. Aggarwal, K.: Mössbauer Studies, in Thin Films and Amorphous Materials. Ph.D. Thesis, I. I. T. Delhi, 1976.
19. Mott, N. F. and Davis, E. A.: Electronic Processes in Non-Crystalline Materials. Clarendon Press, Oxford, 1971, Phil. Mag., vol. 22, 1970, p. 903.
20. Preston, R. S., Lam, D. J., Nevitt, M. V., Van Osterburg, D. O., and Kimball, C. W.: Phys. Rev., vol. 149, 1966, p. 440.
21. Chopra, K. L.: Thin Film Phenomena. McGraw-Hill Book Company, New York, 1969.
22. Wade, R. H. and Silcox, J.: Phys. Stat. Solidi, vol. 19, no. 57, 1967, p. 63.
23. Pashley D. W.: Advac. Phys., vol. 14, 1965, p. 361.


APPROVAL

BULK AND THIN FILMS OF FeTe: A MÖSSBAUER STUDY

By W. T. Escue, Kamna Aggarwal, and R. G. Mendiratta

The information in this report has been reviewed for security classification. The report, in its entirety, has been determined to be unclassified and contains no information concerning Department of Defense or Atomic Energy Commission programs.

This document has also been reviewed and approved for technical accuracy.


for F. BROOKS MOORE
Director, Electronics and Control Laboratory